Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Chemistry 4 (2012) 268 – 274

Procedia Chemistry

Alteration of Bacterial Cellulose Properties by Diacetylglycerol

M. Karina[a,*], L. Indrarti[a], R. Yudianti[a], Indriyati[a], A. Syampurwadi[a]

[a]*Research Center for Physics, Indonesian Institute of Sciences, Jalan Sangkuriang 21/154D, Kompleks LIPI, Bandung 40135, Indonesia*

Abstract

Bacterial cellulose (BC) was altered by means of 0.5-2.5% w/v diacetylglycerol in acetone-water through impregnation process provided DGBC composites. Results from the scanning electron microscope images, revealed that diacetylglycerol filled the pores of BC, leads to the significant enhanced in hydrophilicity and caused a smoother BC morphology. The addition of diacetylglycerol into BC caused a slightly changed in crystallinity indexes and bring about the reduction in tensile strength and Young's modulus but increased in elongation at break and toughness. The significant reduction of tensile strength and Young's modulus was achieved for DGBC 2.5% as well as for elongation at break and hydrophylicity improvement. Through the impregnation method, diacetylglycerol serves as biodegradable and safe plasticizer, resulted in less rigid and higher ductility DGBC composites.

Keywords: Bacterial cellulose; biocomposites; diacetylglycerol; impregnation; mechanical properties.

1. Introduction

Bacterial cellulose (BC) is a cellulose produced by micro-organism activity of *Acetobacter xylinum* (*Gluconacetobacter xylinum*) [1]. Different from plant-derived cellulose, BC is highly pure cellulose content since its free interconnection with hemicelluloses, pectin, and lignin. BC also has no cavity as shown by plant-originated cellulose. As a natural polymer, BC shows superior and unique properties, such as high crystalinity index, high water holding capacity, excellence biocompatibility, and ultrafine network structure. Therefore, BC is a promising material and it has received a great deal of attention for research and applications [2,3]. BC has been used in various applications for electronic paper displays [4], optically transparent composites [5], medical applications [6], and paper making [7]. Several synthetic

* Corresponding author. Tel.: +62-22-2503052; fax: +62-22-2503050
E-mail address: myrtha.karina.sancoyorini@lipi.go.id

doi:10.1016/j.proche.2012.06.037

polymeric materials has been reinforced with BC for composite preparation such as with thermoplastic starch [8,9], phenol formaldehyde [10], polyethylene oxide [11], and polyester with rayon fiber [12].

To enlarge the fields of its applications, modification of BC by joining with other materials has been studied elsewhere. Various substances have been directly incorporated into the cultural medium. 5% v/v poly(vinyl alcohol) (PVA) solution was either added directly into the medium of the BC growth or impregnated into BC gel [13]. Aloe-vera content of 10-50% was added in to the culture medium for BC [14]. Impregnation of BC with 1.5% chitosan solution in 1% aqueous acetic acid has been done [15]. BC was also produced in the presence of corn and potato starch [16]. However, despite its high tensile strength property, BC is very stiff material which may restrict its much wider applications. For application where ductility is required such as for packaging, ductile and elastic of BC is of interest. Alteration of BC with other substances could be a good method to modify its characteristic.

In this paper, the modification of BC by low molecular additive, serving as plasticizer, will be discussed. Diacetylglycerol was used as additive because it is not classified as dangerous to the environment and biodegradable [17]. Therefore, we purposed to investigate the performance of BC-diacetylglycerol by introducing diacetylglycerol into BC gel through impregnation process. Expectedly, diacetylglycerol plays an important role to increase ductility and impart flexibility, thereby producing BC with enhanced properties. The altered BC was characterized by its morphology and mechanical properties. Crystallinity and water absorption capacity of BC-diacetylglycerol (DGBC) were then examined and compared with those of BC. To our knowledge, modification of BC by diacetylglycerol as biodegradable plasticizer has not been studied.

2. Experiment

2.1. Materials and method

The gel-like pellicles of BC with around 10-mm thick (95% of water content) was prepared using coconut water as the main sources of saccharide containing sucrose, ammonium-sulphate, and acetic acid according to a method described previously [18]. BC was washed thoroughly by running tap water until its pH was neutral, then boiled with NaOH solution (2% w/v) for 1 h to remove its impurities and to eliminate bacterial cells, and finally washed with water until its pH was 7.

A commercial diacetylglycerol $C_3H_5OH(CH_3COO)_2$, clear oily liquid, odorless, specific gravity of 1.18 - 1.195 g mL^{-1}, was purchased from Aldrich. In order to make miscible in BC, diacetylglycerol was dissolved in acetone and water (50% v/v). A concentration of 0-2.5% w/v of diacetylglycerol solution in acetone-water was prepared by stirring it for 5 min at room temperature. Treatment of the gel-like pellicles of BC with diacetylglycerol was performed after removal of water by squeezing and freeze dried. A sample of 1 g of freeze dried BC gel was soaked with 100 mL diacetylglycerol solution in room temperature allowing the diacetylglycerol molecules to penetrate BC. Prior to characterization, the sample was then freeze dried.

2.2. Scanning electron microscope observation

The morphology of modified BC was observed using a JEOL Model JSM-6360LA. The specimen was cut and prepared under liquid nitrogen and mounted to an aluminum holder with double-sided carbon tape, then sputter coated with a thin gold layer and observed at an acceleration voltage of 20 kV.

2.3. Mechanical properties testing

Mechanical strength test was performed according to ISO 527 on a Universal Testing Machine (Orientec UCT-5T) using 5 specimens at speed of 10 mm/min. Prior to mechanical properties test, samples were shaped to dumbbell and conditioned at 23 °C, RH 50% for a minimum 40 h.

2.4. X-ray diffraction (XRD)

X-ray diffraction spectra were detected using scintillation counter and a pulse height analyzer. CuK_α radiation (wavelength of 0.15418 nm) was produced at 40 kV and 30 mA, by a Geiger Flex DXG2 (Rigaku Denki Co., Ltd.). The crystallinity index (*CI*) was calculated from the reflected intensity data with Segal *et al.*'s method [19].

$$CI = (I_{002} - I_{am})/I_{002}$$

Where I_{002} is the maximum intensity of the lattice diffraction from the (020) plane at 2θ =22.5° and I_{am} is the intensity of background scatter measured at 2θ =18°.

2.5. Water absorption capacity

Water absorption capacity of BC and DGBC was determined by weighing the sample after 24 h immersion in water at room temperature. The sample was then removed from water and the excess of water was wiped with tissue paper. Water absorption capacity was calculated as indicated by equation:

$$\text{Water absorption} = [(W_1 - W_0)/W_0] \times 100\%$$

where W_0 and W_1 indicate the sample before and after 24 h of immersion in room temperature, respectively.

3. Results and Discussion

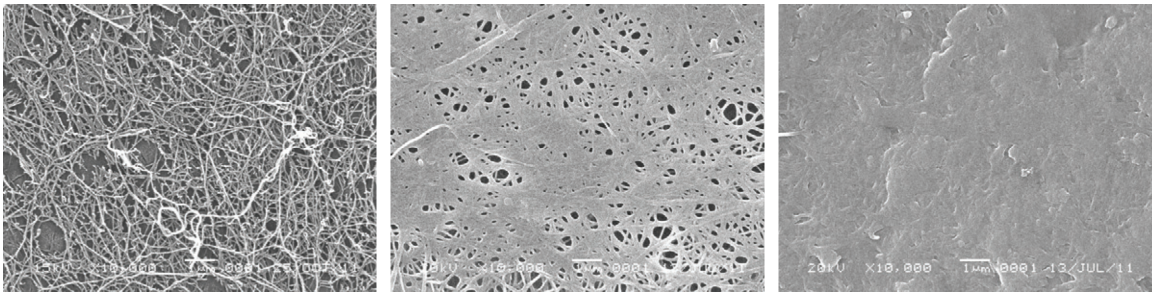
3.1. Scanning electron microscope observation

In current study, the BC gel was treated with diacetylglycerol solution in acetone-water mixture. Expectedly diacetylglycerol coated on the surface, but also penetrate into the BC fiber networks resulting the much softer BC and altered the BC properties. SEM images in Figures 1a-b illustrate the differences in the surface morphology of BC and BC supplemented with 1% w/v of diacetylglycerol.

The addition of diacetylglycerol into BC gel, significantly altered the morphology of BC. Figure 1a shows the surface morphology of BC film, from which continuous network of cellulose fiber are observed. From the surface morphology images of BC-diacetylglycerol as shown in Figure 1b, the introduction of 1% diacetylglycerol into the BC gel, covered the porous cellulose structure. The porous cellulose structure disappeared with the increasing of diacetylglycerol introduction up to 2.5%, Figure 1c.

3.2. Mechanical properties

Mechanical properties are usually involved in end used applications. Therefore, the effect of diacetylglycerol in tensile strength, Young's modulus, elongation at break, and toughness is evaluated. Figure 2 shows the tensile strength of DGBC as a function of diacetylglycerol content. It clearly shows that the treatment of BC with diacetylglycerol altered their tensile strength property. The tensile strength of BC reduced with increasing of diacetylglycerol. Tensile strength of BC at the average thickness of 0.20 µm was 128 MPa and dropped drastically to 102 MPa by the addition of 0.5% w/w diacetylglycerol. However, the addition of diacetylglycerol from 1 to 2.5%, caused a gradual reduction of tensile strength of BC from 98 to 79 MPa, respectively. The initial high strength of BC is due to the strong hydrogen bond among the cellulose fibrils. The presence of diacetylglycerol as an external phase at those concentrations from 0.5 to 2.5% could weaken the hydrogen bonding, resulted the reduction of tensile strength [20].



(a) **(b)** **(c)**

Fig. 1. Scanning electron microscope image surface morphology of (a) BC 0%, (b) DGBC 1% and (c) DGBC 2.5%

The presence of diacetylglycerol affected the fracture work of DGBC. As indicated in Figure 3, fracture work of BC increased with increasing of diacetylglycerol. Fracture work of BC was 34.1 kJ/m^2 and improved drastically almost by the factor of 3, became 97.4 kJ/m^2 and increased gradually from the addition of diacetylglycerol from 1.5 to 2.5%. The fracture work of BC indicates the toughness property. Figure 3 indicates that the addition of diacetylglycerol improve the toughness of BC.

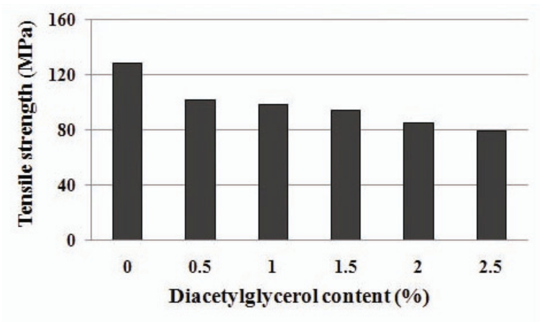


Fig. 2. Tensile strength of BC and DGBC

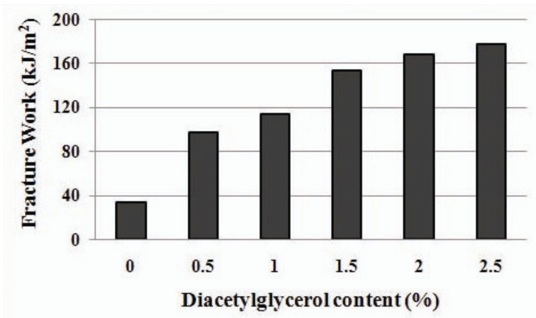


Fig. 3. Fracture work of BC and DGBC

The reduction of Young's modulus of DGBC as a function of diacetylglycerol content was similar with that of tensile strength, Figure 4 in which Young's modulus of BC decreased as diacetylglycerol content increasing. The Young's modulus of BC was 9.400 MPa whereas Young's modulus of DGBC 0.5-2.5% was dropped to 5.700-2.800. The decrease of Young's modulus also means the decreasing of stiffness.

However, different from tensile strength and Young's modulus, the addition of diacetylglycerol increased the elongation at break of BC. Impregnation of diacetylglycerol of 0.5 % w/w slightly increased elongation at break of BC, from 1.3 to 2.3%, Figure 5. Noticeably, the addition of diacetylglycerol up to 2.5% w/w increased the elongation at break significantly by the factor of six, becoming 6.1%, providing the increase of ductility.

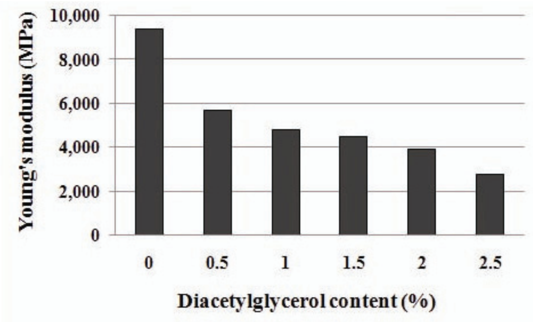


Fig. 4. Young's modulus of BC and DGBC

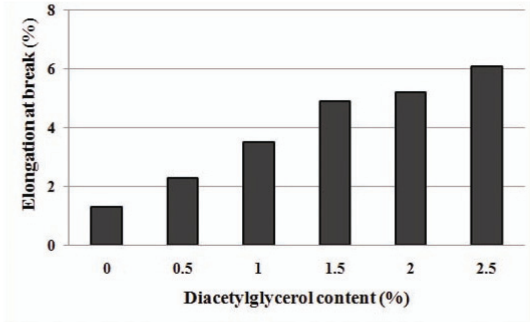


Fig. 5. Elongation at break of BC and DGBC

From the mechanical test showed above it indicates that the presence of diacetylglycerol in BC serves as plasticizer, interrupting hydrogen bonding of cellulose fibrils in BC structure and resulted in reduction in Young's modulus and an increase in elasticity and toughness. This result showed the similarity with the results of that BC treated with PVA by in-situ process in which PVA serves as plasticizer [13]. Even though PVA completely water soluble whereas diacetylglycerol slightly soluble in water, both treatment to BC resulted in improvement of elongation at break.

3.3. XRD analysis

The peaks observed at 2θ = 14.2, 16.7, and 22.5° related with the $(1\bar{1}0)$, (110) and (200) reflections planes of cellulose I, similar with that of plant-based cellulose, Figure 6. These peaks are typical of BC diffractogram [13]. Even though the diffractograms pattern of DGBC showed no difference from that of BC, the introduction of diacetylglycerol decreased the crystallinity, Table 1. The crystallinity of BC is 89%, slightly higher than that of DGBC whereas, the average crystallinity index of DGBC 0.5-2.5% is 87-86%. The lowering of crystallinity might be due to the denser structure of BC and the intermolecular reaction between BC and diacetylglycerol, which causes BC molecular chains difficult to orientation [14]. The decrease in crystallinity will in turn leads to a decrease in the modulus and strength. On the other hand, the function of diacetylglycerol as a plasticizer would increase the elongation at break due to the more space for BC chains when applying stress [21]. Subjection of diacetylglycerol as natural plasticizer limits the crystallinity in BC and increases the free volume present in the BC structure. Thus, increasing the amount of diacetylglycerol as natural plasticizer in the BC gives a more flexible material.

Table 1. Crystallinity index of BC and DGBC

Sample	***CI***
BC	89.79
DGBC 0.5%	87.50
DGBC 1%	87.50
DGBC 1.5%	86.95
DGBC 2%	86.27
DGBC 2.5%	84.31

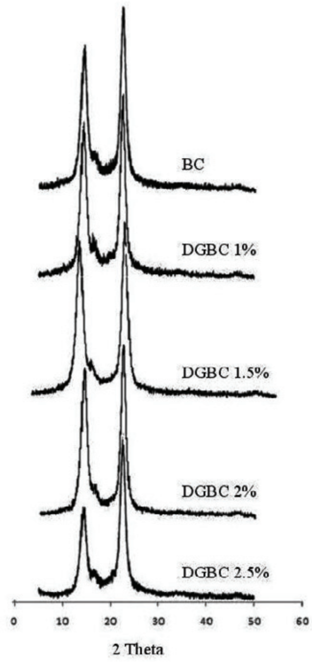


Fig. 6. X-ray diffractogram of BC and DGBC

3.4. Water absorption capacity

Water absorption capacity of BC and DGBC is shown in Figure 7. Water absorption capability of BC increased with the increasing of diacetylglycerol. The addition of diacetylglycerol to 0.5% increased water absorption of BC significantly becoming 14.3% and getting much higher to 37.7 and 41% when the diacetylglycerol added up to 2 and 2.5%, respectively. The increase of water absorption of BC was not only caused by the fact that BC is easily attracts water but also by the addition of the hydrophylic substance. Diacetylglycerol has properties of both glycerol and acetate which is unusually hydrophilic and easily absorbs water molecules into BC. The absorption of diacetylglycerol altered the water absorption capacity of BC significantly.

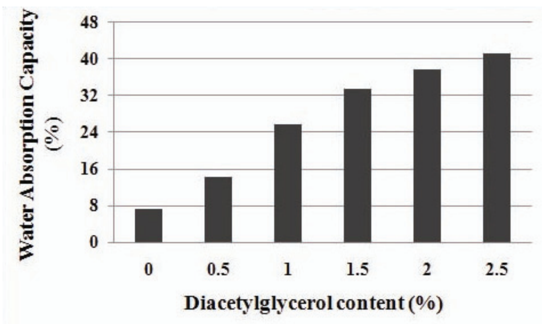


Fig. 7. Water absorption capacity of BC and DGBC

4. Conclusion

Bacterial cellulose (BC) has been modified by means of direct addition of diacetylglycerol solution through impregnation process provided new diacetylglycerol-BC (DGBC). The existence of diacetyl-glycerol in the BC serves a plasticizer. Scanning electron microscope image demonstrated that diacetylglycerol filled the pores and displayed the smoother of BC surface. Distinctly, tensile strength and Young's modulus in DGBC decreased but increasing in elongation at break and fracture of work resulted in reduction in stiffness and increased in ductility and toughness. The lessening in the tensile strength and Young's modulus were dependent on the degree of diacetylglycerol supplement. Increasing amount of diacetylglycerol causes in the slightly reduction of crystallinity. Water absorption capacity increased with the increasing of diacetylglycerol and BC becoming more hidrophylic. Further investigation of BC membrane for edible food packaging is being conducted.

Acknowledgement

The authors would like to acknowledge the funding supported by Research Incentive Program from Directorate General of High Education Department of National Education and Indonesian Institute of Sciences, Grant No. 25/SU/SP/Inst/Ristek/IV/10.

References

[1] Iguchi, M., Yamanaka, S., Budhiono, *J. Mat. Sci*. 2000; **35**: 261-270.

[2] Eichhorn S.J., Dufresne A., Aranguren A., Marcovich N.E., Capadona J.R., Rowan S.J., Weder C., Thielemans W., Roman M., Renneckar S., Gindl W., Weigel, S., Yano H., Abe K., Nogi M., Nakagaito A.N., Mangalam A., Simonsen J., Benight A.S., Bismarck A., Berglund L.A., Peijs, T., *J. Mater. Sci.* 2010; **45**(1): 1-33.

[3] Chen P., Cho S.Y., Jin H.J., *Macromol. Res.* 2010; **18**(4): 309-320.

[4] Shah J.R., Brown M., *J. Appl. Microbiol. Biotechnol.* 2005; **66**: 352-355

[5] Ifuku S., Nogi M., Abe K., Handa K., Nakatsubo F., Yano H., *Biomacromol.* 2007; **8**: 1973-1978.

[6] Kim J., Cai Z., Ce Y., *J. Nanotechnol. Eng. Med*. 2010; **1**(1): 11006-11012.

[7] Basta A.H., Saied E.H., *J. Appl. Microbiol.* 2009; **107**(6): 2098-2107.

[8] Martins I.M.G., Magina S.P., Oliveira L., Freire C.S.R., Silvestre A.J.D., Neto C.P., Gandini A., *Compos. Sci. Technol.* 2009; **69**: 2163-2168

[9] Wan Y.Z., Luo H., He F., Liang H., Huang Y., Li X.L., *Compos. Sci. Technol.* 2009; **69**: 1212-1217.

[10] Nakagaito A.N., Iwamoto S., Yano H., *Appl. Phys. A* 2005; **80**: 93-97.

[11] Brown E., Laborie M.P.G., *Biomacromol.* 2007; **8**: 3074-3081.

[12] Johnson D.C., Neogi A.N., Non Woven Fabric-Like Product Using a Bacterial Cellulose Binder and Method for Its Preparation. *US Patents* 1990, 4,919,753.

[13] Soykeabkaew N., Sian C., Gea S., Peijs T., *Cellulose* 2009; **16**: 435-444.

[14] Saibuatong O., Phisalaphong M., *Carbohydr. Polym.* 2010; **79**: 455-460

[15] Phisalaphong M., Jatupaiboon, *Carbohydr. Polym.* 2008; **74**: 482-488.

[16] Grande C.J., Torres F.G., Gomez C.M., Troncoso O.P., Ferrer J.C., Pastor J.M., *Mat. Sci. Eng. C* 2009; **29**: 1098-1104.

[17] Ioelovich M., Figovsky O., Leykin, A. Patent docs 2010. A. 20100233468.

[18] Yudianti R., Indrarti L., *J. Appl. Sci*. 2008; **8**: 177-180.

[19] Browning B.L., Methods of Wood Chemistry. Vol. II, Interscience Publisher: New York; 1967.

[20] Yamanaka S., Watanabe K., Kitamura N., Iguchi M., Mitsuhashi S., Nishi Y., Uryu M., *J. Mater. Sci.* 1989; **24**: 3141-3145.

[21] Cai Z., Kim J., *Cellulose* 2010; **17**: 83-91.